

ЕКСТРУЗИЯ ТІСТА У КІЛЬЦЕВОМУ ШАРІ, ЩО ЗМАЩУЄ

Розглянуто завдання руху тістової маси в каналі з використанням гідродинамічного мастила. Визначена математична модель динамічного стану в'язкої рідини. Складено рівняння спільної течії. Розроблено спосіб безконтактного формування макаронних виробів, що дозволяє знизити практично до нуля тертя в матрицях макаронного преса.

Ключові слова: тістова маса, гідродинамічна змазка, математична модель, в'язка рідина, течія.

Брылёв Евгений Анатольевич, кандидат технических наук, доцент, кафедра оборудования пищевых производств, Днепропетровский государственный технический университет, Украина, e-mail: brulev_dnepr@mail.ru.

Яцук Анна Леонидовна, ассистент, кафедра оборудования пищевых производств, Днепропетровский государственный технический университет, Украина, e-mail: ann-yatsuk@mail.ru.

Брильов Євген Анатолійович, кандидат технічних наук, доцент, кафедра обладнання харчових виробництв, Дніпропетровський державний технічний університет, Україна.

Яцук Анна Леонідівна, асистент, кафедра обладнання харчових виробництв, Дніпропетровський державний технічний університет, Україна.

Brylov Eugen, Dniprodzerzhinsk State Technical University, Ukraine, e-mail: brulev_dnepr@mail.ru.

Yatsuk Anna, Dniprodzerzhinsk State Technical University, Ukraine, e-mail: ann-yatsuk@mail.ru

УДК 54.058

**Бутенко Е. О.,
Капустін О. Є.**

ЗАХИСТ ВОДНОГО БАСЕЙНУ ВІД ЗАБРУДНЕНИХ СУЛЬФІДНИХ ВОД

Вивчено видалення сульфідів зі стічних вод цеху шлакопереробки, розроблена технологія видалення забруднюючих речовин, побудована установка видалення сульфідів, яка дозволила уникнути забруднення навколишнього середовища та штрафних платежів у розмірі 140 млн. грн. на рік. Оптимізовано умови видалення сульфідів зі стічних вод. Досліджено різні умови синтезів аніонних сорбентів різних типів, а також обговорені різні технології одержання сорбентів в промисловості.

Ключові слова: сульфіді, стічні води, сорбенти, синтетичні аніонні глини, металургійні шлаки, сорбція.

1. Introduction

Sulfides including hydrogen sulfide, are acutely second class of substances of danger. They are highly toxic, inhalation of air containing hydrogen sulfide causes dizziness, headache, nausea, and a considerable concentration leads to coma, convulsions, pulmonary edema and even death. At high concentrations, a single inhalation exposure may cause instant death. The main source of exposure of sulfides in water pool Azov region are smelters. Around smelters are many storage metallurgical slags (Fig. 1). Within the city there are nine waterworks, which are influenced by metallurgical slag.



Fig. 1. Slag repository metallurgical plant, water with a high content of sulfides

Wherever there is a metallurgical slag accumulated in the reservoirs of water with an extremely high concentration of sulfides, which sometimes erupt into streams and rivers, as a result of floods, which leads heavily polluted, the emergence of industrial accidents.

Oxygen in the water is consumed for the oxidation of sulphides, the oxygen content in waters sulphide data becomes zero, and this leads to the destruction of living organisms. Sites for storage of metallurgical slag plant, located near the river Kalchyk. Rivers and lakes occurring near shlagrepository contaminated and turned into storage with contaminated water in which the concentration of sulfides reaches 1 g/l. Although close to the river and located Kalchyk dams, but under emergency breakthroughs often occurs getting polluted water into the river Kalchyk that leads to the death of the inhabitants of the river. Protection dams and oxygen in the air oxidation of sulfides reduce their concentration, but at the final stage, when they are released into natural water bodies, it is necessary to complete removal of sulfides from wastewater. The presence of sulfides in water makes water an unpleasant smell intensifies the process of corrosion of pipelines and their causes overgrowth due to the development of sulfur bacteria. Sulfides have a toxic effect on human and cause skin irritation. Hydrogen sulphide is toxic to living organisms. Prolonged use of water containing the substances at concentrations above regulatory, may develop chronic intoxication, leading eventually to a certain pathology. Note also that the toxic effects of the substances can be shown not only by oral admission of water, but absorbed

through the skin. At high concentrations of hydrogen sulfide a headache, dizziness, insomnia, weakness. There is also a general neurotoxic effect [1]. Maximum permissible concentration of sulphide in water is 0,001 mg/l [2].

The aim of our work was the creation and implementation of technology sulfide removal from wastewater shlagrepository metallurgical plant in order to prevent environmental pollution.

2. Experimental part

As sorbents ispolzovait dvyonnye layered hydroxides (LDH). Syntheses sorbents were carried out as described in [3–5]. The solution of metal salts $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ with concentrations close to 100 g/l, taken in stoichiometric ratio, was poured with stirring into a solution containing approximately twofold excess of alkali carbonates (final pH is 8–10). As a precipitant solution using NaOH and Na_2CO_3 . The deposition time was 24 hours, the crystallization at a temperature of 80 °C was 96 hours. The resulting samples were washed until no alkaline reaction, and dried at 120 °C to constant weight.

Sulfides determined by reacting the sulfide oxidation products with N,N-dimethyl-n-phenylenediamine salt of Fe^{3+} in acidic medium to form methylene blue. Volumetric flask was placed 40,0 ml 100,0 ml of distilled water is then added 20,0 ml of the filtered solution samples were analyzed, as well poured 10,0 ml of 0,1 mol/l zinc acetate, 2,5 ml of 0,5 % solution of N,N-dimethyl-p-phenylenediamine and 1,0 ml of 5 % FeCl_3 and adjusted to the mark with water. The flask was stoppered, stirred for 30 seconds. The flask was heated on a water bath for 5 minutes. The absorbance of the obtained solution was measured at a wavelength of 670 nm. Used cell length of 50 mm. Reference solution – water. Preliminarily investigated the rate of air oxidation of hydrogen sulfide. Calibration curve for the determination of sulphides photocolometric. Sorption studies were performed in batch conditions, loading the sorbent in a solution containing contaminants (sulfides) and sampled after stirring vigorously for a while. Standard sorbate concentration amounted to: $\text{S}^{2-} = 5 \cdot 10^{-4}$ mol/l.

3. Laboratory investigations

Research sorption of sulfide ions LDH performed in stirred tank reactor with periodic sampling, the concentration of sulfide ions was determined spectrophotometrically. The data obtained revealed that the rate of sorption sulphides high, the system quickly reaches a state of equilibrium. Were determined by calculation of the first order rate constant of sorption of sulfide ions with different masses of the sorbent. The resulting kinetic dependence of sorption suggests the first order by weight of the sorbent. To replace sorbents mass concentration of active centers in the bulk solution using dynamic capacitance values for all LDH defined in terms of dynamic equilibrium. To determine the activation parameters sorption of sulfide ions was studied on LDH leakage of ion exchange at different temperatures. Were determined rate constants for sorption of sulfide ions at different temperatures. The resulting value of the activation energy indicates that the reaction occurs in the diffusion area, but close enough to the kinetic energy, which means high acidity of sulfide ions.

Full kinetic equation for the sorption of sulfide ions sorbent $\text{Mg}/(\text{Mg} + \text{Al}) = 0,72$ mol/mol has the form: $k = 0,5 \cdot 10^3 \cdot e^{-23280/RT}$, $\vartheta = 0,5 \cdot 10^3 \cdot e^{-23280/RT} \cdot C_{\text{S}^{2-}} \cdot C_{\text{a.s.}}$. The study of sorption processes for different composition LDH possible to determine the rate constants of the second order for the sorption of sulfide ions. On the basis of kinetic regularities sorption process parameters were calculated install pollution prevention sulfide environment. This setting is implemented on shlagrepositories metallurgical plant, Mariupol [6–9].

4. Technology calculation sulfides removal unit

Practical results were implemented in a plant for the removal sulfides at the metallurgical plant. Industrial cleaning Kalchyk riverbed and water purification, storage near metallurgical slag, used LDH obtained on an industrial scale. The ratio $\text{Mg}/\text{Mg} + \text{Al}$ is 0,72 mol/mol, the surface area is 150–200 m^2/g , a tablet of 5 mm diameter and 5 mm thick. Initial data for calculation of adsorption unit were as follows. Rainfall draining through the slag conversion accumulate in natural depressions separated from the river dam. With very heavy rain or emergency water breaks through the dam and the creek falls into the river. Maximum water flow in the creek in the shop is 50 m^3/hr shlag concentration of sulfides in the mouth of the creek – 12 mg/l, which is $4 \cdot 10^{-4}$ mol/l. To clean river tableted using layered double hydroxides with a ratio $\text{Mg}/\text{Mg} + \text{Al} = 0,72$ mol/mol. Sorption rate sulphides described by the equation: $\vartheta = k \cdot C_{\text{S}^{2-}} \cdot C_{\text{a.s.}}$, where k – rate constant of the second order, $\text{l/mol} \cdot \text{s}$, $k = 245,4 \text{ l/mol} \cdot \text{s}$, Cs^{2-} – the concentration of sulphides in the stream flowing into the river from the territory slag conversion. $\text{S}^{2-} = 12 \text{ mg/dm}^3$, or $4 \cdot 10^{-4}$ mol/l. The concentration of active sites is calculated by: $C_{\text{a.s.}} = E \cdot \frac{m}{V}$, where $E = 0,163 \text{ meq/g}$. Taking into account that the pelletized sorbent porosity is 50 %, we find that the effective concentration of the active sites: $C_{\text{a.s.}} = \frac{500}{0,5} \cdot 0,163 = 0,163 \text{ mol/l}$. It was calculated that the residence time in the reactor should be more than 200 (more than three minutes). Choose a normal average fluid velocity in the reactor $\omega = 0,2 \text{ m/s}$. Sectional flow: 0,07 m^2 , the required length of the pipe is: $l = 40 \text{ m}$. Under the terms of terrain pipe will be installed at an angle of 0,7/10, mean estimated speed of 0,3 m/s, which is close to the calculated value, the turbulent regime will be provided. For convenience, the service was installed trough cut from the pipeline axis. Its diameter is: $d = 0,5 \text{ m}$. To reduce the length of the tube, while maintaining the efficiency of its work, it is proposed to increase the flow path of water through tangential deflection. Total pipe length is 10 m Total sorbent for water is 75 kg [10]. Sorption capacity used granular anionic clay was 0,16 meq/g. Therefore, 1 kg of sorbent absorbs $16,3 \cdot 10^{-3}$ equivalents sulfides that is: 0,261 g/kg. The initial concentration of sulfides was 12,0 and finite – 0,4 mg/l. From these data we find that one can purify sorbent kg 22,4 dm^3 wastewater contaminated with sulfides. Taking into account that the cost of granular sorbent is 50 €/ton, calculated the cost of cleaning 1 m^3 of wastewater contaminated with sulfides is 2,22 €. These data are important to compare with the size of damages caused by nature, due to the discharge of pollutants into

bodies of water with sewage. Calculating the size of damages caused by water bodies (except sea water) due to the emission of pollutants from wastewater in excess of the established limit values [5]. Penalty payments for 1 ton of pollutants (sulfides) will be: 7029900 uan/ton. Cleaning cost of 1 ton of synthetic anionic clays sulfides is: 16667 €. It is approximately 183 333 uan/t. Thus, cost-effective use of sorbents proposed because it costs significantly less than the penalty payments for enterprise environment contamination sulfides.

We estimate the size of the penalty payments that would have paid the company, if this setting was not built in a shop shlakopererabotki. Water flow in the stream is 50 m³/hr, the concentration of sulfides — 12 mg/l. Annual discharge sulfides be 5,265 tonnes and penalty payments amount to 140 mln.

5. Conclusions

1. The investigations on the removal of sulfides from wastewater metallurgical plant.
2. A technology that prevents pollution runoff shlagrepository.
3. Designed and built the installation remove sulfides in the slag conversion in the metallurgical plant.
4. Plant operation prevented penalties for environmental pollution in the amount of 140 mln. per year.

Література

1. Мирнюк, Д. Я. Современное состояние и проблема качества воды водоисточников Донбасса [Текст] / Д. Я. Мирнюк, Е. А. Запорожская // Вестник гигиены и эпидемиологии. — 1998. — Т. 2, № 1. — С. 23–24.
2. ДСанПІН 2.2.7.029-99. Гігієнічні вимоги щодо поводження з промисловими відходами та визначення їх класу небезпеки для здоров'я населення [Текст]. — К., 1999. — 6 с.
3. Капустин, А. Е. Неорганические аниониты [Текст] / А. Е. Капустин // Успехи химии. — 1991. — Т. 60, № 12. — С. 2685–2717.
4. Reichle, W. T. Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcites) [Text] / W. T. Reichle // Solid State Ionics. — 1986. — № 22. — P. 135–141.
5. Бутенко, Э. О. Синтез и технология получения анионных адсорбентов [Текст] / Э. О. Бутенко, А. Е. Капустин // Восточно-Европейский журнал передовых технологий. — 2010. — № 2/6(44). — С. 41–47.
6. Бутенко, Э. О. Разработка технологии очистки сбросных вод при помощи анионных сорбентов [Текст] / Э. О. Бутенко, А. Е. Капустин, А. В. Смотров, М. П. Снитко // VIII международная научно-техническая конференция молодых специалистов, Юрьевка, 29–31 августа 2008. — Мариуполь, 2008. — С. 95–97.
7. Бутенко, Э. О. Разработка технологии удаления сульфидов из сточных вод шлакопереработки [Текст] / Э. О. Бутенко, А. В. Смотров, А. Е. Капустин, М. П. Снитко // VIII международная научно-техническая конференция молодых специалистов, Юрьевка, 29–31 августа 2008. — Мариуполь, 2008. — С. 98–100.
8. Бутенко, Э. О. Селективная сорбция анионных соединений глинистыми минералами различного состава [Текст] / Э. О. Бутенко, А. Е. Капустин // Современный научный вестник. — Белгород, 2009. — № 27(53). — С. 105–110.
9. Butenko, E. The adsorption of sulfide ions by clay minerals [Text] / E. Butenko, A. Kapustin, R. Guegan // XIV International Clay Conference, Castellana Marina, Italy, 14–20 June 2009. — Bari, Italy, 2009. — V. 2. — P. 286.
10. Бутенко, Э. О. Сорбционное удаление токсических соединений из промышленных сточных вод при помощи слоистых двойных гидроксидов [Текст] : сб. науч. статей / Э. О. Бутенко, А. Е. Капустин // Экология и здоровье человека, охрана воздушного и водного бассейнов. — Харьков, 2010. — Т. 2. — С. 315–325.
11. Про затвердження методики розрахунку розмірів відшкодування збитків, заподіяних державі внаслідок порушення законодавства про охорону та раціональне використання водних ресурсів [Текст] : наказ Міністерства охорони навколишнього середовища України № 389 від 20.07.2009. — С. 171–181.

ЗАЩИТА ВОДНОГО БАССЕЙНА ОТ ЗАГРЯЗНЕННЫХ СУЛЬФИДНЫХ ВОД

Изучено удаление сульфидов из сточных вод цеха шлакопереработки, разработана технология удаления загрязняющих веществ, построена установка удаления сульфидов, которая позволила избежать загрязнения окружающей среды и штрафных платежей в размере 140 млн. грн. в год. Оптимизированы условия удаления сульфидов из сточных вод. Исследованы различные условия синтезов анионных сорбентов различных типов, а также обсуждены различные технологии получения сорбентов в промышленности.

Ключевые слова: сульфиды, сточные воды, сорбенты, синтетические анионные глины, металлургические шлаки, сорбция.

Бутенко Елеонора Олегівна, кандидат технічних наук, доцент, кафедра охорони довкілля та раціонального природокористування, Маріупольський державний гуманітарний інститут, Україна, e-mail: butenkoeo@rambler.ru.

Капустин Олексій Євгенович, доктор хімічних наук, професор, завідувач кафедри хімічної технології та інженерії, Приазовський державний технічний університет, Україна, e-mail: kapustin_a_e@pstu.edu.

Бутенко Элеонора Олеговна, кандидат технических наук, доцент, кафедра охраны окружающей среды и рационального природопользования, Мариупольский государственный гуманитарный институт, Украина.

Капустин Алексей Евгеньевич, доктор химических наук, профессор, заведующий кафедрой химической технологии и инженерии, Приазовский государственный технический университет, Украина.

Butenko Eleonora, Mariupol State Humanitarian Institute, Ukraine, e-mail: butenkoeo@rambler.ru.

Kapustin Alexey, Pryazovskyi State Technical University, Ukraine, e-mail: kapustin_a_e@pstu.edu